

# Nucleus-independent chemical shift (NICS) profiles in a series of monocyclic planar inorganic compounds

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## Abstract

A series of monocyclic planar inorganic compounds have been optimized at the B3LYP/6-311+G\* level. GIAO-B3LYP nucleus-independent chemical shifts (NICS) profiles calculated in the perpendicular direction of each ring show that the series of analyzed compounds can be classified in three groups according to their aromatic, non-aromatic or antiaromatic character. Our results suggest exercising caution in the use of single-point NICS calculations as a quantitative measure of aromaticity for these species.

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## 1. Introduction

In 2001, Boldyrev, Wang, and co-workers, observed for the first time aromaticity in  $Al_4^{2-}$ , an all-metal compound [1]. Since then, a large number of inorganic clusters with aromatic properties have been synthesized while some others have just been investigated from a theoretical point of view (for two recent reviews, see Ref. [2]). As compared to the classical aromatic organic molecules that possess only  $\pi$  electron delocalization, the aromaticity in inorganic clusters is more complex. These compounds have  $\sigma$ - and  $\pi$ - (or even  $\delta$ - [3]) electron delocalization, thus giving rise to the so-called multifold aromaticity [4,5].

A paradigmatic case is the metalloaromaticity of  $Al_4^{2-}$  and related clusters.  $Al_4^{2-}$  contains a pair of delocalized  $\pi$ -electrons and two pairs of  $\sigma$ -electrons that contribute to the overall aromaticity of this species [1,6,7]. The two  $\pi$ -electrons obey the  $4n + 2$  Hückel rule for monocyclic  $\pi$ -systems [8]. Although this is not the case for the  $\sigma$ -electrons, it was found that the two pairs of delocalized

$\sigma$ -electrons belong to molecular orbitals that follow orthogonal radial and tangential directions, which makes them to be totally independent [9], thus separately following the  $4n + 2$  rule. This is a clear example that simple total electronic counts do not provide necessarily direct evidence of the aromaticity or antiaromaticity of these all-metal aromatic systems [10]. We can briefly add here that in planar polycyclic boron clusters it has been found that the aromaticity is neither related to the total number of  $\pi$ -electrons [11].

Therefore, while the  $4n + 2$  rule affords a simple test, aromaticity is a much complex phenomenon [12], especially in all-metal systems [2]. According to Schleyer and Jiao [13], aromatic systems are conjugated cyclic  $\pi$ -electron (and/or  $\sigma$ - and  $\delta$ -electron in all-metal species) compounds that exhibit cyclic electron delocalization leading to bond length equalization, abnormal chemical shifts and magnetic anisotropies, and energetic stabilization. In view of that, the evaluation of aromaticity is usually based on the classical aromaticity criteria: structural, magnetic, energetic, and reactivity-based measures [14,15]. In addition, measures of local aromaticity based on the analysis of electron delocalization have been recently proposed [16,17]. As a

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consequence of the multidimensional character of aromaticity [14,18], it is found that different criteria of aromaticity may signal different overall conclusions [19]. For this reason, the use of differently based aromaticity criteria is recommended [19–21].

Indeed, the aromaticity of  $\text{Al}_4^{2-}$  has been confirmed by four generally accepted criteria for aromaticity: energetic (resonance energies [9]), structural (planarity with equal bond lengths [1]), magnetic (ring currents [7,10] and nucleus-independent chemical shifts (NICS) values [2,4]) and electronic (ELF plots [17] and hardness and polarizability values [22]). Although initially the aromaticity of  $\text{Al}_4^{2-}$  was attributed to the two  $\pi$ -electron system [1], it is now well recognized that the contribution to aromaticity coming from the four  $\sigma$ -electrons is more important than the  $\pi$  one [7,9,10,17].

Probably the most widely employed method to analyze the aromaticity of all-metal species is the NICS index. This descriptor of aromaticity was proposed by Schleyer et al. [23] as a magnetic index of aromaticity. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system, usually above the ring center. Rings with large negative NICS values are considered aromatic. The more negative the NICS values, the more aromatic the rings are. Non-aromatic species have NICS values close to zero and positive NICS values are indicative of antiaromaticity. NICS is usually computed at ring centers (NICS(0)) determined by the non-weighted mean of the heavy atoms coordinates. But it also can be calculated at certain distance above or below the center of the ring taken into analysis. In fact, the NICS obtained at 1 Å above the molecular plane (NICS(1)) [24] is considered to better reflect the  $\pi$ -electron effects than NICS(0).

It is worth noting that the maximum negative value of NICS is found at the center of the  $\text{Al}_4^{2-}$  ring (NICS(0)), while the maximum one for benzene is at about 1 Å above the center of the ring (NICS(1)). For this reason, it has been suggested that the NICS(0) are better suited for evaluation of the aromaticity for all-metal species [4]. However, it may be the case that NICS(0) is appropriate for systems having larger  $\sigma$  than  $\pi$ -aromaticity (such as  $\text{Al}_4^{2-}$ ,  $\text{Al}_2\text{Si}_2$  [4], or  $\text{H}_3^+$  [25]), while NICS(1) may be more appropriated for systems with more important  $\pi$ -aromatic character (such as benzene or  $\text{Mg}_3\text{Na}_2$  [26]). In addition, it has been shown that maps of ring currents change significantly with the distance between the plotted and molecular planes [10]. Thus, being NICS an integrated property of the current density maps [27], one can expect important changes of the NICS values computed at different distances to the molecular plane. The aim of this work is to discuss the change of NICS with distance in the direction perpendicular to the molecular plane for different systems and see whether there are some common trends in the NICS profiles of these species. To this end, we have plotted the NICS profiles for a large series (55 species) of inorganic monocyclic planar (or almost planar) aromatic, non-aromatic, and antiaro-

matic systems. The results will allow us to decide whether it is better to use NICS(0) or NICS(1) or instead, the full profile is needed to compare and discuss aromaticity in inorganic aromatic species. A similar analysis could be performed with the aromatic ring current shieldings (ARCS) approach that uses NICS profiles to derive the strength of the induced aromatic ring current and the size of the ring [28]. It has been shown for a series of organic species that ARCS is very suitable to detect molecular aromaticity [28].

We are aware of the fact that since NICS is an integrated property of the current density maps [27], in particular cases, this indicator of aromaticity may induce misleading conclusions in organic [20,29] and inorganic aromatic species [25]. However, NICS is, in general, a valuable indicator of aromaticity that is used by many researchers to discuss aromaticity. In this sense, we think it is worth to analyze its profile behavior for this series of 55 simple monocyclic planar inorganic systems.

## 2. Computational details

All calculations reported in this work were performed by means of the GAUSSIAN 98 [30] computational package. The gas-phase optimized geometries reported here were calculated in the framework of density-functional theory (DFT) using the B3LYP functional [31] which combines the three-parameter Becke's exchange non-local functional [32] and the transformed form [33] of Lee–Yang–Parr's correlation non-local functional [34]. The 6-311+G\* basis set [35] was used for all calculations. To ensure that a minimum on the potential energy surface (PES) was obtained under the imposed constraint of the indicated symmetry (cf. second column of Table 1), we carried out vibrational frequency calculations at the same level, B3LYP/6-311+G\*.

NICS values were also computed with the B3LYP/6-311+G\* method through the gauge-including atomic orbital method (GIAO) [36] implemented in GAUSSIAN 98. The magnetic shielding tensor was calculated for ghost atoms located at the ring critical point (RCP), the point of lowest density in the ring plane [37], as suggested by Cossio et al. [38]. These values are denoted as NICS(0), according to the practice described by Schleyer et al. [23] who calculated the NICS at the geometrical center (GC) of the ring. Due to the high symmetry of the molecules studied, both points RCP and GC, usually coincide. Similarly, NICS values at 1.0 Å above the perpendicular plane of the ring, NICS(1) [39], as well as the NICS(1)<sub>zz</sub> tensor component have been calculated. This latter quantity gives probably the best measure of aromaticity among the different NICS related definitions [40]. These values of NICS(1) and NICS(1)<sub>zz</sub> were calculated with the aim to measure the aromaticity due to  $\pi$ -system, sometimes obscured by the  $\sigma$ -current when NICS is calculated within the molecular plane.

Although most of the molecules have all their atoms contained in a single plane, some species studied are not completely planar. For these non-planar molecules, the best fitted plane  $\pi$  (obtained by minimizing the distances

Table 1

Collection of B3LYP/6-311+G\* NICS values (in ppm) calculated at the ring center, NICS(0), 1.0 Å above its ring, NICS(1), and the tensor *z*-component of the latter, NICS<sub>zz</sub>(1), for the optimized B3LYP/6-311+G\* ground state geometry of each species

System		NICS(0)	NICS(1)	NICS <sub>zz</sub> (1)
Al <sub>3</sub> <sup>-</sup>	D <sub>3h</sub> /1A <sub>1</sub> '	-35.8	-26.7	-30.6
Al <sub>4</sub> <sup>-</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	-34.5	-27.4	-54.9
Al <sub>2</sub> Si <sub>2</sub>	D <sub>2h</sub> /1A <sub>g</sub>	-11.7	-16.9	-35.5
As <sub>4</sub> <sup>2-</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	8.5	4.1	21.9
As <sub>5</sub> <sup>-</sup>	D <sub>5h</sub> /1A <sub>1</sub> '	-15.3 (-20.5) <sup>a</sup>	-14.6 (-19.5) <sup>a</sup>	-33.9
B <sub>4</sub>	D <sub>2h</sub> /1A <sub>g</sub>	-35.7 <sup>b</sup>	-9.1 <sup>b</sup>	4.8
B <sub>4</sub> <sup>+</sup>	D <sub>2h</sub> /2A <sub>g</sub>	-33.4 <sup>b</sup>	-6.6 <sup>b</sup>	1.9
B <sub>4</sub> <sup>-</sup>	D <sub>2h</sub> /2A <sub>g</sub>	-42.0 <sup>b</sup>	-19.2 <sup>b</sup>	-27.0
B <sub>5</sub>	C <sub>2v</sub> /2B <sub>2</sub>	-17.1 <sup>c</sup>	-14.1	-21.1
B <sub>5</sub> <sup>+</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-36.2 <sup>c</sup>	-18.8	-24.3
B <sub>5</sub> <sup>-</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-7.3 <sup>c</sup>	-13.8	-22.3
B <sub>6</sub>	C <sub>2h</sub> /1A <sub>g</sub>	-23.3	-1.9	8.8
B <sub>6</sub> <sup>2-</sup>	D <sub>2h</sub> /1A <sub>g</sub>	-3.6 (-4.2) <sup>d</sup>	8.9 (9.0) <sup>d</sup>	29.0
B <sub>2</sub> Si <sub>2</sub>	D <sub>2h</sub> /1A <sub>g</sub>	-42.0	-29.1	-57.2
B <sub>2</sub> Si <sub>2</sub> <sup>+</sup>	D <sub>2h</sub> /2A <sub>g</sub>	-39.8	-21.3	-36.5
B <sub>2</sub> Si <sub>2</sub> <sup>2+</sup>	D <sub>2h</sub> /1A <sub>g</sub>	-25.7	-0.7	19.4
B <sub>4</sub> Si <sub>3</sub>	C <sub>2v</sub> /1A <sub>1</sub>	-9.2	-2.8	8.3
B <sub>4</sub> Si <sub>2</sub> <sup>2+</sup>	D <sub>2h</sub> /1A <sub>g</sub>	-13.3	-8.5	-15.7
Be <sub>5</sub>	D <sub>5h</sub> /1A <sub>1</sub> '	13.1 <sup>e</sup>	5.8 <sup>e</sup>	-15.7
Be <sub>5</sub> <sup>-</sup>	D <sub>5h</sub> /2A <sub>2</sub> '	-4.8 <sup>e</sup>	-4.6 <sup>e</sup>	-23.6
Be <sub>2</sub> Al <sub>3</sub> <sup>+</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-24.5	-19.0	-32.1
Be <sub>3</sub> Al <sub>2</sub> <sup>+</sup>	C <sub>2v</sub> /2B <sub>1</sub>	-10.3	-8.4	-27.9
Be <sub>3</sub> Al <sub>2</sub> <sup>2+</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-0.8	-2.2	-25.4
Be <sub>4</sub> Al <sub>2</sub> <sup>2+</sup>	D <sub>2h</sub> /1A <sub>g</sub>	13.0	10.0	12.3
Be <sub>2</sub> Si <sub>2</sub>	D <sub>2h</sub> /1A <sub>g</sub>	-22.4	-12.6	-8.2
Be <sub>2</sub> Si <sub>2</sub> <sup>-</sup>	D <sub>2h</sub> /2A <sub>g</sub>	-28.2	-19.8	-33.8
Be <sub>2</sub> Si <sub>2</sub> <sup>2-</sup>	D <sub>2h</sub> /1A <sub>g</sub>	-33.5	-24.9	-53.9
Be <sub>3</sub> Si <sub>2</sub>	C <sub>2v</sub> /1A <sub>1</sub>	-30.3	-21.7	-36.8
C <sub>3</sub> B <sub>4</sub>	C <sub>2v</sub> /1A <sub>1</sub>	-22.6	-12.4	-19.3
C <sub>2</sub> N <sub>2</sub> <sup>+</sup>	C <sub>s</sub> /2A''	-28.8	-14.6	-23.1
C <sub>3</sub> N <sub>3</sub> <sup>+</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-18.7	-18.7	-34.9
C <sub>3</sub> N <sub>2</sub> <sup>-</sup>	C <sub>2v</sub> /2B <sub>2</sub>	-14.0	-4.7	-11.7
C <sub>3</sub> N <sub>3</sub> <sup>2+</sup>	D <sub>3h</sub> /2A <sub>1</sub> '	-28.2	-15.7	-38.4
Ga <sub>3</sub> <sup>-</sup>	D <sub>3h</sub> /1A <sub>1</sub> '	-27.3	-22.6	-25.1
Ga <sub>4</sub> <sup>-</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	-39.2	-29.9	-57.7
GeAl <sub>3</sub> <sup>-</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-34.7	-28.5	-56.7
Mg <sub>3</sub>	D <sub>3h</sub> /1A <sub>1</sub> '	-1.0 (1.7) <sup>f</sup>	-1.5 (-1.2) <sup>f</sup>	-7.5
Mg <sub>3</sub> <sup>-</sup>	D <sub>3h</sub> /2A <sub>2</sub> '	-0.2	-2.6	-14.6
Mg <sub>3</sub> <sup>2-</sup>	D <sub>3h</sub> /1A <sub>1</sub> '	-2.8	-4.0	-12.2
Mg <sub>4</sub> <sup>2+</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	-10.7	-8.6	-25.7
Mg <sub>2</sub> Al <sub>3</sub> <sup>+</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-4.8	-10.8	-46.3
Mg <sub>2</sub> Si <sub>2</sub> <sup>2-</sup>	C <sub>s</sub> /1A'	-24.1	-21.9	-49.1
Mg <sub>3</sub> Si <sub>2</sub> <sup>2+</sup>	C <sub>s</sub> /1A'	-33.4	-17.3	-16.8
N <sub>4</sub> <sup>2-</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	4.0	-1.5	-8.6
N <sub>5</sub> <sup>-</sup>	D <sub>5h</sub> /1A <sub>1</sub> '	-16.5	-16.5	-45.2
P <sub>4</sub> <sup>2-</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	9.6	3.7	17.6
P <sub>5</sub> <sup>-</sup>	D <sub>5h</sub> /1A <sub>1</sub> '	-16.6 (-18.5 <sup>a</sup> , -22.0 <sup>g</sup> )	-15.8 (-18.3) <sup>a</sup>	-39.2
S <sub>4</sub> <sup>2+</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	2.1 (-10.6) <sup>a</sup>	-0.5 (-7.9) <sup>a</sup>	9.0
S <sub>2</sub> N <sub>2</sub>	D <sub>2h</sub> /1A <sub>g</sub>	3.6 (-2.6) <sup>a</sup>	-1.4 (-4.7) <sup>a</sup>	1.1
S <sub>4</sub> N <sub>3</sub> <sup>+</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-10.0 (-12.1) <sup>a</sup>	-8.8 (-10.7) <sup>a</sup>	-21.0
S <sub>4</sub> N <sub>4</sub> <sup>2+</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	-17.4 (-20.6) <sup>a</sup>	-14.7 (-17.0) <sup>a</sup>	-41.5
Se <sub>4</sub> <sup>2+</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	-3.1 (-9.8) <sup>a</sup>	-2.2 (-7.6) <sup>a</sup>	6.9
Si <sub>3</sub> <sup>2+</sup>	D <sub>3h</sub> /1A <sub>1</sub> '	-28.0	-21.6	-30.5
Si <sub>4</sub> <sup>2+</sup>	D <sub>4h</sub> /1A <sub>1g</sub>	-42.0	-28.8	-58.0
SiAl <sub>5</sub> <sup>-</sup>	C <sub>2v</sub> /1A <sub>1</sub>	-33.9	-26.3	-52.5

Calculated values reported from the literature are pointed out in parenthesis.

<sup>a</sup> Ref. [43]. Differences can be ascribed to the use of GIAO and CTOCD methods.

<sup>b</sup> In this work and in Ref. [45].

<sup>c</sup> In this work and in Ref. [47].

<sup>d</sup> Ref. [49].

<sup>e</sup> In this work and in Ref. [50].

<sup>f</sup> Ref. [26].

<sup>g</sup> Ref. [46].

of nuclear positions of the atoms in the ring to the plane  $\pi$ ) has been calculated [41] in order to find the perpendicular direction (the  $z$ -axis hereafter) to the molecular ring.

### 3. Results and discussion

We have studied 55 inorganic systems which, in some cases ( $\text{Al}_4^{2-}$ ,  $\text{Al}_2\text{Si}_2$ ,  $\text{As}_5^-$ ,  $\text{B}_6^{2-}$ ,  $\text{Be}_5$ ,  $\text{Be}_5^-$ ,  $\text{Mg}_3^{2-}$ ,  $\text{P}_4^{2-}$ ,  $\text{P}_5^-$ ,  $\text{S}_4^{2+}$ ,  $\text{Se}_4^{2+}$ ,  $\text{Si}_4^{2+}$ ,  $\text{S}_2\text{N}_2$ ,  $\text{S}_4\text{N}_3^+$ , and  $\text{S}_4\text{N}_4^{2+}$ ), have been already reported in the literature [1,2,4,5,7,9–12,26,42–50], while to our knowledge the rest are reported for the first time. Geometry optimizations have been performed at the symmetry and electronic state (the ground state in all cases) indicated in Table 1 for each system. Table 1 also contains the values of NICS(0), NICS(1), and NICS(1) $_{zz}$  for the molecular systems studied within its symmetry and electronic state. These results are in line with those already reported by De Proft et al. [43], for some of the molecules studied in this paper ( $\text{As}_5^-$ ,  $\text{P}_5^-$ ,  $\text{S}_4^{2+}$ ,  $\text{Se}_4^{2+}$ ,  $\text{S}_2\text{N}_2$ ,  $\text{S}_4\text{N}_3^+$ , and  $\text{S}_4\text{N}_4^{2+}$ ).

Let us begin with the comparison between the different NICS values. A plot of the NICS(0) versus the NICS(1) values gives a correlation of  $r^2 = 0.689$ . Not unexpectedly, the correlation between the NICS(1) and NICS(1) $_{zz}$  is better ( $r^2 = 0.745$ ). However, there is almost no correlation between the NICS(0) and NICS(1) $_{zz}$  values ( $r^2 = 0.325$ ). This is an indication that these two NICS values measure rather different effects. It is likely that the NICS(1) $_{zz}$  values accounts mainly for the  $\pi$  aromaticity effects, while NICS(0) results better reflect both the  $\sigma$  and  $\pi$  aromaticity or antiaromaticity effects. As a result, the correlation between these two NICS values is rather low.

As an attempt to discuss the use of NICS as a measure of aromaticity for inorganic compounds, we have plotted NICS values along the  $z$ -axis to the ring plane beginning on the center of the molecular ring up to 5.0 Å. We have found that the shape of NICS profiles with respect to the distance from the ring center falls into three categories; the three profiles are depicted in Fig. 1. In addition, for all species, we have localized the NICS maxima and minima and determined the distances to the center of the ring at which they occur. The results are reported in Table 2 and the plots for all the species are given in the Supporting Information. Table 3 contains the classification we find for the studied species in the three afore-mentioned categories.

The first class labeled as “I” follows a monotonically ascent for the regular cases, showing the highest absolute value of NICS close to the center of the ring. One would anticipate *aromatic character* for the species belonging to this group. Although all molecules in this category are expected to be aromatic, one can notice a different range of behaviors. Some species exhibit NICS maxima near the ring center, while some others have a maximum about 0.5 Å to the ring center or farther, and the rest have a quite constant NICS between 0 and 0.5 Å, showing an intermediate situation. It is likely that induced magnetic fields generated by the  $\sigma$  aromaticity (for instance, in  $\text{Al}_4^{2-}$  where  $\sigma$

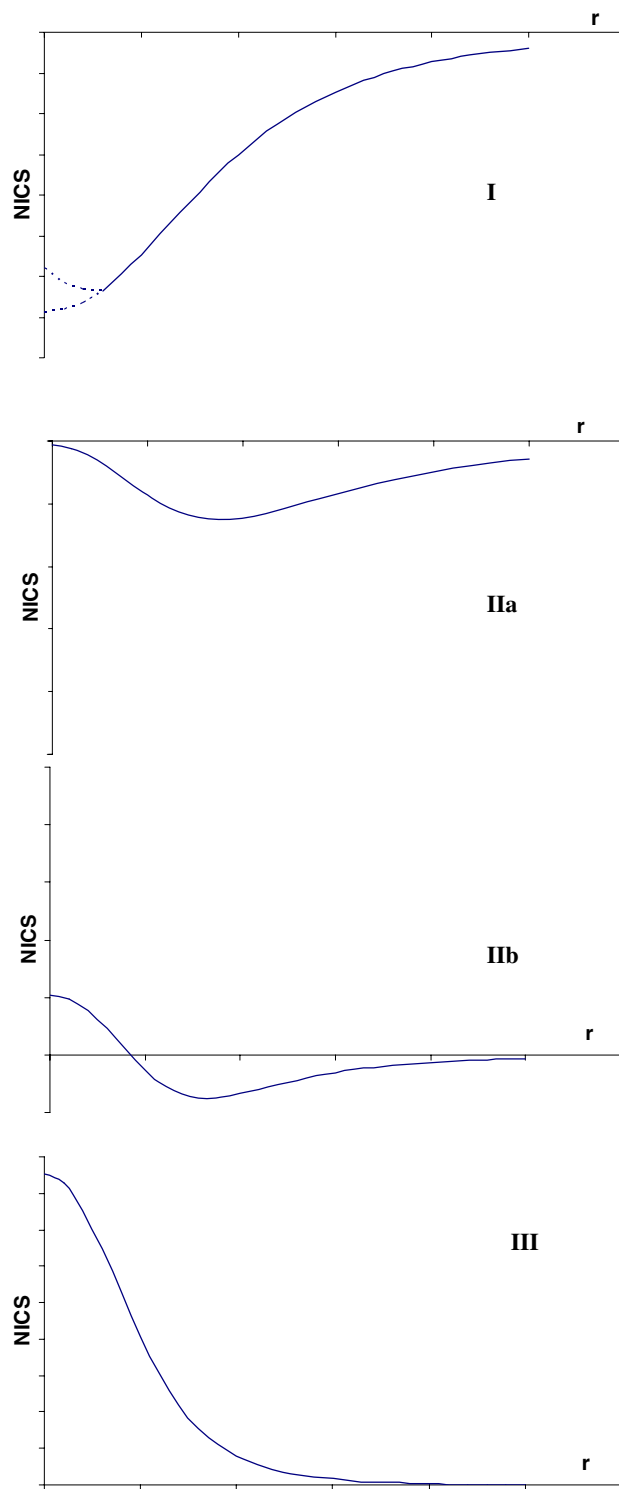


Fig. 1. Schematic plots of the NICS values from the ring critical point up to 5 Å above the ring following an axis perpendicular to the ring plane. Three different kinds of behavior are observed, labeled as I, II(a,b), and III.

aromaticity is more important than the  $\pi$  one [7,9,10,17]) are particularly large in the center of the ring, whereas systems having  $\pi$  aromaticity show a minimum NICS at certain distances from the center of the ring, like in benzene (for comparison purposes we have included in Table 2

Table 2

Maximum and minimum (bold) values of NICS along  $z$ -axis direction perpendicular to the center of the ring plane of the studied systems calculated at B3LYP/6-311+G\* level of theory

System	# of maximum	# of minimum	NICS	$R^a$
Al <sub>3</sub> <sup>-</sup>	0	1	-35.76	0.0
Al <sub>4</sub> <sup>2-</sup>	0	1	-34.45	0.0
Al <sub>2</sub> Si <sub>2</sub>	1	2	-11.69, -17.02	0.0, 0.88
As <sub>4</sub> <sup>2-</sup>	1	0	8.53	0.0
As <sub>5</sub> <sup>-</sup>	1	2	-15.30, -15.45	0.0, 0.5
B <sub>4</sub>	2	1	1.35, -35.68	2.34, 0.0
B <sub>4</sub> <sup>+</sup>	2	1	1.68, -33.36	2.08, 0.0
B <sub>4</sub> <sup>-</sup>	0	1	-42.04	0.0
B <sub>5</sub>	1	2	-17.09, -19.96	0.0, 0.5
B <sub>5</sub> <sup>-</sup>	0	1	-36.17	0.0
B <sub>5</sub> <sup>-</sup>	1	2	-7.27, -16.28	0.0, 0.68
B <sub>6</sub>	2	1	1.62, -23.26	1.76, 0.0
B <sub>6</sub> <sup>2-</sup>	2	1	8.96, -3.58	1.08, 0.0
B <sub>2</sub> Si <sub>2</sub>	0	1	-41.98	0.0
B <sub>2</sub> Si <sub>2</sub> <sup>+</sup>	0	1	-39.76	0.0
B <sub>2</sub> Si <sub>2</sub> <sup>2+</sup>	2	1	-3.69, -25.67	1.6, 0.0
B <sub>4</sub> Si <sub>2</sub> <sup>2+</sup>	1	2	-13.33, -13.47	0.0, 0.18
B <sub>4</sub> Si <sub>3</sub>	2	1	-0.95, 9.21	2.02, 0.0
Be <sub>5</sub>	1	2	13.11, -0.54	0.0, 3.15
Be <sub>5</sub> <sup>-</sup>	1	2	-4.78, -4.87	0.0, 0.54
Be <sub>2</sub> Al <sub>3</sub> <sup>+</sup>	0	1	-24.49	0.0
Be <sub>3</sub> Al <sub>3</sub> <sup>+</sup>	0	1	-10.31	0.0
Be <sub>3</sub> Al <sub>2</sub> <sup>2+</sup>	1	2	-0.83, -3.02	0.0, 1.58
Be <sub>4</sub> Al <sub>2</sub> <sup>2+</sup>	0	1	-12.96	0.0
Be <sub>2</sub> Si <sub>2</sub>	2	1	-0.12, -22.39	3.9, 0.0
Be <sub>2</sub> Si <sub>2</sub> <sup>-</sup>	0	1	-28.19	0.0
Be <sub>2</sub> Si <sub>2</sub> <sup>2-</sup>	0	1	-33.52	0.0
Be <sub>3</sub> Si <sub>2</sub>	0	1	-30.28	0.0
C <sub>3</sub> B <sub>4</sub>	0	1	-22.57	0.0
C <sub>2</sub> N <sub>2</sub> <sup>+</sup>	1	2	-28.81, -29.97	0.0, 0.54
C <sub>3</sub> N <sub>2</sub> <sup>+</sup>	1	2	-18.69, -26.72	0.0, 0.56
C <sub>3</sub> N <sub>2</sub> <sup>-</sup>	0	1	-13.98	0.0
C <sub>3</sub> N <sub>3</sub> <sup>2+</sup>	0	1	-28.15	0.0
Ga <sub>3</sub> <sup>-</sup>	0	1	-27.29	0.0
Ga <sub>4</sub> <sup>2-</sup>	0	1	-39.18	0.0
GeAl <sub>3</sub> <sup>-</sup>	0	1	-34.73	0.0
Mg <sub>3</sub>	1	2	-1.04, -1.55	0.0, 1.4
Mg <sub>3</sub> <sup>-</sup>	1	2	-0.20, -3.74	0.0, 1.8
Mg <sub>3</sub> <sup>2-</sup>	1	2	-2.84, -4.38	0.0, 1.6
Mg <sub>4</sub> <sup>2+</sup>	0	1	-10.67	0.0
Mg <sub>2</sub> Al <sub>3</sub> <sup>+</sup>	1	2	-4.78, -11.46	0.0, 1.46
Mg <sub>2</sub> Si <sub>2</sub> <sup>-</sup>	1	2	-24.13, -24.70	0.0, 0.66
Mg <sub>3</sub> Si <sub>2</sub> <sup>2+</sup>	2	1	-0.29, 33.37	3.54, 0.0
N <sub>4</sub> <sup>2-</sup>	1	2	-4.05, 1.53	0.0, 1.0
N <sub>5</sub> <sup>-</sup>	1	2	-16.49, -19.63	0.0, 0.6
P <sub>4</sub> <sup>2-</sup>	1	2	9.64, -0.49	0.0, 2.74
P <sub>5</sub> <sup>-</sup>	1	2	-16.65, -16.86	0.0, 0.5
S <sub>4</sub> <sup>2+</sup>	1	2	2.09, -1.49	0.0, 1.6
S <sub>2</sub> N <sub>2</sub>	1	2	3.61, -1.668	0.0, 1.2
S <sub>4</sub> N <sub>3</sub> <sup>+</sup>	0	1	-10.04	0.0
S <sub>4</sub> N <sub>4</sub> <sup>2+</sup>	0	1	-17.38	0.0
Se <sub>4</sub> <sup>2+</sup>	0	1	-3.09	0.0
Si <sub>2</sub> <sup>2+</sup>	1	2	-27.96, -28.78	0.0, 0.38
Si <sub>4</sub> <sup>2+</sup>	0	1	-42.02	0.0
SiAl <sub>3</sub> <sup>-</sup>	0	1	-33.91	0.0
C <sub>4</sub> H <sub>4</sub> <sup>-</sup>	2	3	1.05, -14.51, -1.37	1.54, 0.0, 3.4
C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	0	1	-12.52	0.0
C <sub>6</sub> H <sub>6</sub>	1	2	-7.91, -10.47	0.0, 0.8

<sup>a</sup> Distance (in Å) from the ring critical point to the NICS minimum or maximum.

Table 3

Classification of each studied molecule according to the behavior shown in Fig. 1. It is pointed out in parenthesis, the number of valence  $\sigma$ - and  $\pi$ -electrons, respectively, for each species

<i>I</i> (aromatic)		<i>IIa</i> (low aromatic)		<i>IIb</i> (non-aromatic)		<i>III</i> (antiaromatic)	
Al <sub>3</sub> <sup>-</sup>	(8,2)	Be <sub>5</sub> <sup>-</sup>	(10,1)	N <sub>4</sub> <sup>2-</sup>	(16,6)	As <sub>5</sub> <sup>2-</sup>	(22,6)
Al <sub>4</sub> <sup>2-</sup>	(12,2)	Be <sub>3</sub> Al <sub>2</sub> <sup>2+</sup>	(10,2)	S <sub>4</sub> <sup>2+</sup>	(16,6)	B <sub>6</sub> <sup>2-</sup>	(16,4)
Al <sub>2</sub> Si <sub>2</sub>	(12,2)	Mg <sub>3</sub>	(6,0)	S <sub>2</sub> N <sub>2</sub>	(16,6)	Be <sub>5</sub>	(10,0)
As <sub>5</sub> <sup>-</sup>	(20,6)	Mg <sub>3</sub> <sup>-</sup>	(7,1)			Be <sub>4</sub> Al <sub>2</sub> <sup>2+</sup>	(12,0)
B <sub>4</sub>	(10,2)	Mg <sub>3</sub> <sup>2-</sup>	(8,2)			P <sub>4</sub> <sup>2-</sup>	(16,6)
B <sub>4</sub> <sup>+</sup>	(9,2)	Se <sub>4</sub> <sup>2+</sup>	(16,6)				
B <sub>4</sub> <sup>-</sup>	(11,2)						
B <sub>5</sub>	(13,2)						
B <sub>5</sub> <sup>+</sup>	(12,2)						
B <sub>5</sub> <sup>-</sup>	(14,2)						
B <sub>6</sub>	(14,4)						
B <sub>2</sub> Si <sub>2</sub>	(12,2)						
B <sub>2</sub> Si <sub>2</sub> <sup>+</sup>	(11,2)						
B <sub>2</sub> Si <sub>2</sub> <sup>2+</sup>	(10,2)						
B <sub>4</sub> Si <sub>2</sub> <sup>2+</sup>	(16,2)						
B <sub>4</sub> Si <sub>3</sub>	(20,4)						
Be <sub>2</sub> Al <sub>3</sub> <sup>+</sup>	(10,2)						
Be <sub>2</sub> Si <sub>2</sub>	(10,2)						
Be <sub>2</sub> Si <sub>2</sub> <sup>-</sup>	(11,2)						
Be <sub>3</sub> Al <sub>2</sub> <sup>+</sup>	(10,1)						
Be <sub>3</sub> Si <sub>2</sub>	(12,2)						
C <sub>3</sub> B <sub>4</sub>	(18,6)						
C <sub>2</sub> N <sub>2</sub> <sup>+</sup>	(14,3)						
C <sub>3</sub> N <sub>2</sub> <sup>+</sup>	(14,2)						
C <sub>3</sub> N <sub>2</sub> <sup>-</sup>	(17,6)						
C <sub>3</sub> N <sub>3</sub> <sup>2+</sup>	(19,6)						
Ga <sub>3</sub> <sup>-</sup>	(8,2)						
Ga <sub>4</sub> <sup>2-</sup>	(12,2)						
GeAl <sub>3</sub> <sup>-</sup>	(6,2)						
Mg <sub>2</sub> Al <sub>3</sub> <sup>+</sup>	(12,0)						
Mg <sub>2</sub> Si <sub>2</sub> <sup>2-</sup>	(12,2)						
Mg <sub>3</sub> Si <sub>2</sub> <sup>2+</sup>	(10,2)						
Mg <sub>3</sub> Si <sub>2</sub> <sup>2+</sup>	(10,2)						
Mg <sub>4</sub> Si <sub>2</sub> <sup>2+</sup>	(32,10)						
N <sub>5</sub> <sup>-</sup>	(20,6)						
P <sub>5</sub> <sup>-</sup>	(20,6)						
Si <sub>3</sub> <sup>2+</sup>	(8,2)						
Si <sub>4</sub> <sup>2+</sup>	(12,2)						
SiAl <sub>3</sub> <sup>-</sup>	(12,2)						
S <sub>4</sub> N <sub>3</sub> <sup>+</sup>	(28,10)						
S <sub>4</sub> N <sub>4</sub> <sup>2+</sup>	(32,10)						

the values for three well-characterized organic systems [23,51]: C<sub>6</sub>H<sub>6</sub> (D<sub>6h</sub>), C<sub>5</sub>H<sub>5</sub><sup>-</sup> (D<sub>5h</sub>) and C<sub>4</sub>H<sub>4</sub><sup>2-</sup> (D<sub>4h</sub>), all calculated at the current level of theory). Besides, the value of the maximum differs significantly from system to system.

Class “II” stands for non-aromatic or low-aromatic compounds; the molecules in this group have *low aromaticity if any*. Depending on whether the molecules are slightly aromatic or antiaromatic, the compounds in this group fall into two subcategories: those that are closer to aromatic behavior, “IIa”, and those that have a rather antiaromatic character, “IIb”. Molecules in “IIa” class have a slightly negative NICS value throughout the profile, while those in “IIb” change from low positive to low negative values as the distance increases.

Category “III” starts from large and positive NICS values and goes to non-aromatic NICS values (close to 0), at large distances from the ring center. Therefore, this category includes the *antiaromatic* class of compounds.

As shown before, the position of the minimum in the NICS profile changes for the different species. Not only the position of the minimum but also the absolute NICS value at a given distance is quite different and in some cases unexpected results are obtained. For instance, one would predict a decrease in aromaticity when going from Al<sub>4</sub><sup>2-</sup> to GeAl<sub>3</sub><sup>-</sup> due to reduction of symmetry. However, according to the NICS(0) values, the GeAl<sub>3</sub><sup>-</sup> species is slightly more aromatic than the isoelectronic Al<sub>4</sub><sup>2-</sup> system. More expected are the NICS profiles showing that Al<sub>2</sub>Si<sub>2</sub> is quite less aromatic than SiAl<sub>3</sub><sup>-</sup> and this, in turn, slightly less aromatic than Al<sub>4</sub><sup>2-</sup>. These results seem to indicate that if one substitutes an Al atom in Al<sub>4</sub><sup>2-</sup> by an atom of a different



row from the periodic table, such as Ge, then the calculated NICS profiles cannot be directly compared to discuss whether a system is more aromatic than another.

Systems like  $S_4^{2+}$ ,  $Se_4^{2+}$ , and  $S_2N_2$  [12,43], having both aromatic  $\pi$  and antiaromatic  $\sigma$  character, are grouped into category **II**, apparently because the antiaromatic character in these cases compensates or even prevails over the aromatic effects. The antiaromaticity of  $Be_5$  and the non-aromatic character of  $Be_5^-$  being discussed by Zhao et al. [50] are also corroborated by our NICS profiles. Finally, most boron clusters [45,47–49,52] are hereby found as aromatic, with the exception of  $B_6^-$  [42,49], which exhibits a typical antiaromatic profile. However, it is worth mentioning some differences among the aromatic boron clusters:  $B_6$ ,  $B_4$ , and  $B_4^+$  rapidly decay to NICS zero values, a symptom that their aromaticity is mainly  $\sigma$ -like, while  $B_5^+$  and  $B_4^-$  decay more slowly to zero, as if their  $\pi$ -aromaticity were somehow more important than in the former. On the other hand,  $B_5^-$  and  $B_5$  NICS profiles goes through lower NICS values, and have a clear minimum near the 1 Å, especially in  $B_5^-$ , probably an indication of its higher  $\pi$ -aromaticity with respect to other boron clusters.

Although we have been unable to derive general rules, some trends are revealed as empirical rules drawn from the results of our classification. Thus, it seems that: (1) molecules having twelve  $\sigma$ -electrons and two  $\pi$ -electrons and those containing twenty  $\sigma$ - and six  $\pi$ -electrons, respectively, always fall in the aromatic group **I**; (2) molecules having sixteen  $\sigma$ - and six  $\pi$ -electrons, are definitely not aromatic (which is to say, non-aromatic or even antiaromatic).

In general, a notable reduction in the NICS values is observed when the size of the ring increases (compare for instance the NICS values of the following series of pairs of systems:  $B_5^+ < B_4^+$ ,  $Ga_4^{2-} < Ga_3^-$ ,  $Mg_4^{2+} < Mg_3$ ,  $N_5^- < N_4^{2-}$ ,  $P_5^- < P_4^{2-}$ , and  $Si_4^{2+} < Si_3^{2+}$ ). This effect was also reported by Schleyer et al. [53] when comparing the NICS values of benzene and  $Si_6H_6$  and those of  $N_6$  and  $P_6$ . Furthermore, there are some exceptions to this size-of-ring rule, namely  $B_5 > B_4$  and  $B_5^- > B_4$ . Be as it may, it is clear that the ring size has an important influence on the NICS values. However, it is not possible to quantify how much of the NICS change in these cases must be attributed to the different ring size or to the change in electronic structure when going from one system to another. In this context, the ARCS approach could be useful since it provides a way to calculate the radius of the ring current loop from the NICS profiles [28].

In summary, we have seen that monocyclic inorganic planar species can be classified into three categories according to the shape of the NICS profiles. In this sense, NICS profiles are useful to decide about the aromatic, non-aromatic or antiaromatic character of a given monocyclic inorganic compound. This is because NICS values are, in general, effective probes for the dia- and paratropicity of ring currents associated with aromatic and antiaromatic behavior. However, these NICS profiles are highly dependent, both qualitatively and quantitatively, on the type of

aromaticity present ( $\sigma$ ,  $\pi$  or even  $\delta$ ), the size of the ring, and the nature of the atoms involved (isoelectronic systems with atoms belonging to different rows may yield significantly different profiles). The large differences found in the NICS profiles of inorganic aromatic species reflect the multiple kinds of aromaticity that can be present in these systems as a result of a more complicated electronic structure than that of their organic counterparts. This makes the comparison of aromaticity between different inorganic aromatic species much more difficult, if not probably unrealistic. Although NICS can still give a qualitative picture of aromaticity, we do not think that a single-point NICS value (or even the whole NICS profile) can be used to decide whether the aromaticity of a given inorganic system is larger than another one with totally different characteristics.

#### 4. Conclusions

To investigate the complex behavior of aromaticity in all-metal species, we have computed the NICS profiles for a large series of monocyclic planar inorganic compounds having aromatic, non-aromatic or antiaromatic character. According to the shape of the NICS profiles, we have classified the analyzed species in three categories **I**, **II**, and **III** that correspond to aromatic, non-aromatic, and antiaromatic species, respectively. While the boundaries between the different categories are somewhat diffuse, it is found that most compounds clearly fall into one of these three categories.

We have shown that neither all NICS minima fall near the ring center nor are located at 1.0 Å of it. Therefore, the widespread NICS(0) and NICS(1) values used in organic species to compare aromaticities between different molecular rings, are not necessarily the best option when dealing with inorganic compounds. In fact, it has been found that NICS profiles (and consequently single-point NICS values) are highly dependent on the ring size, the kind of aromaticity present (i.e., the electronic structure), and the nature of the atoms involved. Therefore, neither single-point NICS values nor full NICS profiles should be used to quantitatively compare the aromaticity between all-metal species with quite different ring size or type of aromaticity or having atoms belonging to different rows of the periodic table.

Finally, since aromaticity is a complicated phenomenon that has multidimensional character, more detailed studies using a set of aromaticity descriptors must be done to better understand the aromaticity manifestations in these inorganic species. Research in this direction is currently under way in our laboratory.

#### 5. Note added in proof

After the present paper was accepted, an interesting work that uses NICS profiles in organic systems as a method to quantify aromaticity was published [54].

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## Appendix A. Supplementary information

B3LYP/6-311+G\* optimized Cartesian *xyz* coordinates and plots of NICS profiles for all the inorganic systems discussed in this work are available and can be found in the online version at doi:10.1016/j.jorganchem.2006.01.038.

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